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(54) Title: ELECTRODEPOSITION OF NICKEL-TUNGSTEN AMORPHOUS AND MICROCRYSTALLINE COATINGS			
(57) Abstract <p>A nickel tungsten-containing coating (30) is electrodeposited onto a substrate (34) from an electrodeposition bath having in solution from about 0.034 to about 0.047 moles per liter of nickel, from about 0.15 to about 0.28 moles per liter of tungsten, from about 0.13 to about 0.43 moles per liter of hydroxycarboxylic acid, and 0 or from about 0.077 to about 0.15 moles per liter of boron. The bath has a pH of from about 6 to about 9, and the electrodeposition is preferably accomplished at a temperature of from about 100 °F to about 140 °F.</p>			

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-1-

Electrodeposition of Nickel-Tungsten
Amorphous and Microcrystalline Coatings

Technical Field

This invention relates to electrodeposited 5 coatings, and, more particularly, to such a coating incorporating nickel, tungsten, and boron and that has high hardness but low residual stress.

Background Art

Coatings are widely used to protect 10 substrates in wear-inducing and/or corrosive environments. Amorphous and microcrystalline materials offer promise for use as protective coatings. An amorphous material has no long-range or short-range crystallographic order, and therefore 15 no grain boundaries that can preferentially erode or corrode. Microcrystalline (including nanocrystalline) materials have very small grains, but have been observed to have excellent erosion and 20 corrosion resistance. Certain types of amorphous and microcrystalline materials also exhibit extremely high hardnesses, making them ideal candidates for protective coatings.

One approach to depositing amorphous and 25 microcrystalline materials as protective coatings is to rapidly solidify a melt against the substrate to be coated. This rapid solidification approach is practiced for some applications, but not for others such as the coating of the insides of tubes.

Another approach is electrodeposition from a 30 bath onto a cathode. One such electrodeposition approach is described in US Patent 4,529,668. According to this process, a boron-containing amorphous alloy is deposited from a bath containing, for example, ions of tungsten, cobalt, and boron. 35 The resulting tungsten-cobalt-boron compound is

-2-

amorphous with a high hardness and wear resistance. It may be deposited on exterior and interior surfaces, uniformly and with great control. The approach of the '688 patent has a deposition rate of 5 about 0.001-0.003 inches in eight hours of deposition. This rate is fully acceptable for many applications, but may be too slow for other coating requirements.

Thus, there is always an ongoing need for 10 techniques to produce desirable coatings at higher deposition rates. The present invention fulfills this need, and further provides related advantages.

Disclosure of Invention

The present invention provides a process for 15 depositing a nickel/tungsten-based coating onto surfaces, and the resulting coating and coated articles. Preferably, the coating also contains boron. The coating is amorphous, microcrystalline (including nanocrystalline), or a mixture of 20 amorphous and microcrystalline, has high hardness and wear resistance, is corrosion resistant, and has low internal residual stress. The coating process is highly efficient, having a coating efficiency of over 40 percent. The coating can be deposited at 25 rates of up to about 0.014 inches in eight hours, over four times the highest rate previously possible for electrodeposited amorphous coatings when deposited at comparable temperatures. It may also be deposited at lower rates and at relatively lower 30 temperatures that are easier to implement commercially in some cases. The coating is resistant to cracking.

In accordance with the invention, an electrodeposition process for depositing a

-3-

nickel-tungsten coating onto a substrate includes the steps of preparing an electrodeposition bath comprising in solution from about 0.034X to about 0.047X moles per liter of nickel, from about 0.15X 5 to about 0.28X moles per liter of tungsten, from about 0.13X to about 0.43X moles per liter of hydroxycarboxylic acid, and 0 or from about 0.077X to about 0.15X moles per liter of boron, the bath having a pH of from about 6 to about 9. The scaling 10 factor X can range from about 0.67 to about 1.7. The bath constituents are provided from bath additions of sources such as salts. A nickel-tungsten coating is electrodeposited onto a substrate from the electrodeposition bath.

15 The resulting coating has a composition in weight percent of about 60 percent nickel, 39 percent tungsten, and 1 percent boron. It has a hardness of about 600 HV (Vicker's Hardness) in the as-plated condition, and the hardness can be 20 increased to 900-1100 HV by heat treating the deposited coating at a temperature of about 600F for four hours. The coating is amorphous, microcrystalline (including nanocrystalline), or a mixture of amorphous and microcrystalline, both when 25 deposited and after heat treating.

The coating of the invention can be deposited on exterior surfaces and also interior surfaces of articles, such as the interior bore of a cylinder. It is highly controllable in deposition rate and 30 final characteristics. Deposition and coating modifiers such as brightening agents (for example, butyne diol) and wetting agents (for example, sodium lauryl sulfate) can be added to the deposition bath, to improve the characteristics of the final coating.

35 The present invention provides an advance in the art of wear-resistant and corrosion-resistant coatings. The coatings are hard, yet have low

-4-

residual stress. Amorphous and microcrystalline coatings can be prepared at relatively high deposition rates. Other features and advantages of the present invention will be apparent from the 5 following more detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention.

Brief Description of The Drawings

10 Figure 1 is a schematic illustration of a preferred electrodeposition apparatus for conducting the process of the invention;

Figure 2 is a schematic side sectional view of a coated substrate;

15 Figure 3 is an X-ray diffraction pattern of a coating that has a mixture of amorphous and nanocrystalline regions;

Figure 4 is an X-ray diffraction pattern of a nanocrystalline coating; and

20 Figure 5 is an X-ray diffraction pattern of a crystalline coating.

Best Mode for Carrying Out The Invention

As illustrated in Figure 1, an electrodeposition process in which the anode is not 25 consumed is typically accomplished in a tank 10 sufficiently large to hold a quantity of an electrodeposition bath 12 containing the elements to be co-deposited. The tank 10 further contains an anode 14 having a positive potential applied thereto 30 and a cathode 16 having a negative potential applied thereto, both immersed in the bath 12. The

-5-

potentials are applied by a power supply 18 having a current capacity sufficient for the size of the cathode 16. In the presently preferred design, the anode 14 is placed in a sealed anode chamber 5 separated from the remainder of the bath 12 by an ion permeable membrane 20, in an approach familiar to those in the art. The bath 12 is preferably gently stirred by a stirrer 22, and may also be mildly agitated by pumping the electrodeposition 10 bath through the tank. Under the influence of the potential applied across the anode 14 and the cathode 16, dissociated positive species migrate toward the cathode 16 and are deposited thereon, while electrons may be visualized as traveling from 15 the cathode 16 to the anode 14 as the electrodeposition current.

The structure illustrated in Figure 1 is the presently preferred apparatus for accomplishing the electrodeposition in accordance with the invention, 20 but use of the present invention is not limited to this apparatus. Other means for electrodepositing the coatings may be utilized. For example, the cathode may become a container for the bath, as, for example, where the electrodeposition bath and anode 25 are placed within the container and the negative potential is applied to the container. The coating is thereafter deposited on the inner bore of the cathode/container. A curved or irregularly shaped anode may be provided to conform to a curved or 30 irregularly shaped cathode, facilitating the deposition of a desired coating on the cathode. Such modifications are known to those skilled in the art, and the present invention is compatible with such apparatus modifications.

35 The structure produced by the present approach is illustrated in Figure 2. A coating 30 of an amorphous-microcrystalline alloy is deposited

onto a surface 32 of a substrate 34. The coating 30 is amorphous, microcrystalline (including nanocrystalline), or a mixture of amorphous and microcrystalline regions. The substrate 34 is made 5 the cathode 16 of the cell depicted in Figure 1 during the electrodeposition process.

The deposition bath 12 is formed from a number of constituents, each selected for its operability in combination with the other 10 constituents. The bath includes a source of nickel ions which may be chosen from a variety of compounds such as nickel oxide, nickel carbonate, nickel sulfate, nickel chloride, or combinations thereof. The source of nickel preferably provides a nickel 15 concentration in the deposition bath of from about 0.034X to about 0.047X moles per liter, most preferably about 0.046X moles per liter. X is a scaling factor that can vary from 0.67 to 1.7, and is selected by the user of the invention. It is 20 used to scale the amounts of all of the constituents of the deposition bath by the same amount, for any particular value of X chosen.

The bath further includes a source of tungsten ions which may be chosen from a variety of 25 compounds such as sodium tungstate, ammonium tungstate, ammonium meta tungstate, tungstic acid, or combinations thereof. The source of tungsten preferably provides a tungsten concentration in the deposition bath of from about 0.15X to about 0.28X 30 moles per liter, most preferably about 0.21X moles per liter.

The bath further includes a source of boron which may be chosen from a variety of compounds such 35 as boron phosphate, boric acid, or combinations thereof. The source of boron preferably provides a boron concentration in the deposition bath of from about 0.077X to about 0.15X moles per liter, most

-7-

preferably about $0.11X$ moles per liter.

The bath further includes a source of a hydroxycarboxylic acid, preferably a citrate or a tartrate, or combinations thereof. The source of 5 hydroxycarboxylic acid preferably provides a hydroxycarboxylic acid concentration of from about 0.13X to about 0.43X moles per liter, most preferably about 0.23X moles per liter for a citrate and about 0.29X moles per liter for a tartrate.

10 In all cases, the same scaling factor X is used to determine the amount of each constituent of the bath. As an example, if the user selected a scaling factor X equal to 1.4, then the preferred concentration of the source of nickel yields a bath 15 nickel content of 0.046 times 1.4 or 0.064 moles per liter; the preferred concentration of the source of tungsten yields a bath tungsten content of 0.21 times 1.4 or 0.29 moles per liter; the preferred concentration of the source of boron yields a bath 20 boron content of 0.11 times 1.4 or 0.15 moles per liter; and the preferred concentration of the source of hydroxycarboxylic acid yields a bath hydroxycarboxylic acid content of 0.23 times 1.4 or 0.32 moles per liter for a citrate.

25 The scaling factor X can vary in the range of from about 0.67 to about 1.7. If X is outside this range, either substantially below or substantially above, the quality of the coating is reduced and becomes unacceptable. Within the range, the 30 selection of a particular value of X is made to achieve particularly preferred properties. For example, characteristics such as deposition efficiency, deposition rate, coating adherence, coating strength, and coating corrosion resistance 35 vary according to the value of the scaling factor selected. In some instances, improved economics of deposition are more important than attaining

-8-

particular physical properties, and in other cases the opposite may be true. The inventors have found that selection of the scaling factor X of 1.4 yields the best mix of desirable coating properties and 5 economic deposition for their requirements.

Bath deposition conditions are generally common to all compositions. The pH of the bath 12 is adjusted to from about 6 to about 9 by the 10 addition of a base such as sodium hydroxide or ammonium hydroxide to the bath. The temperature of the bath during electrodeposition is preferably about 100F-140F. The higher the deposition 15 temperature, the faster the rate of deposition. However, a particular advantage of the present invention is that relatively high deposition rates can be achieved even for relatively low temperatures such as 120F. The applied voltage between the anode 14 and the cathode 16 is typically from about 3 to about 8 volts. The current density at the cathode 20 16 is from about 0.3 to about 1.2 amperes per square inch.

A most-preferred composition of the electrodeposition bath 12 is about 5.8 grams per liter of nickel carbonate, about 70 grams per liter 25 of sodium tungstate, about 53 grams per liter of ammonium citrate monohydrate, and about 6.3 grams per liter of boric acid. The pH is from about 8.4 to about 8.6, and the temperature is about 120F. A secondary most-preferred composition using other 30 sources of species to be deposited is about 13 grams per liter of nickel sulfate hexahydrate, about 70 grams per liter of sodium tungstate, about 50 grams per liter of ammonium citrate, about 12 grams per liter of boron phosphate. The pH is from about 8.4 to about 8.6, and the temperature is about 120F. In 35 each case, the deposition temperature may be increased to increase the deposition rate of the

-9-

coating.

A number of plating characteristics are of interest and importance. The deposition rate is normally preferred to be as great as possible, as 5 the process efficiency is directly related to deposition rate. The rate of thickness buildup of the coating should be as great as possible, consistent with acceptable plating quality and the required hardness. The hardness is related to 10 strength. The hardness tends to predict wear resistance, particularly if the wearing medium is no harder than the plating.

Another important characteristic of the plating is the plating or residual stress in the 15 coating. The lowest residual stress is preferred. When the residual stress is too high, cracking and lifting of the coating from the substrate can be experienced. Where adherence of the coating to the substrate is good, cracking may be acceptable in 20 certain applications, such as some parts of internal combustion engines. However, where corrosion resistance is required, cracking must be avoided completely.

Thus, the preferred electrodeposition bath 25 compositions are those that have deposition rates of at least about 0.4 grams per ampere-hour at a current density of 0.3 amperes per square inch, have a plating thickening rate of at least 19 micrometers per hour, have a minimum microhardness of at least 30 about 900 HV after a 4 hour oven soak at 600F, and exhibit a qualitative plating stress of less than about 30,000 pounds per square inch (tensile) or in certain cases of no more than about 60,000 pounds per square inch (tensile) even at large plating 35 thicknesses and high coating hardness.

A number of samples were prepared and evaluated to establish the limits of the deposition

-10-

parameters and the nature of the results obtained. The following Table I lists the results of these tests. In Table I, column (1) is an Example number for reference. Column (2) is the current density during deposition in amperes per square inch. Columns (3)-(6) express the electrodeposition bath content. Column (3) is the nickel content expressed as moles per liter of nickel supplied as either nickel carbonate (c) or nickel sulfate (s) or nickel chloride (l) or a mixture (m) of nickel carbonate and nickel chloride. Column (4) is the tungsten content expressed as moles per liter of tungsten supplied as sodium tungstate. Column (5) is the hydroxycarboxylic acid (HCA) content expressed as moles per liter of HCA supplied by ammonium citrate (c) or ammonium tartrate (t). Column (6) is the boron content expressed as moles per liter of boron supplied by boric acid (ba) or boron phosphate (bp). Column (7) is the pH of the electrodeposition bath. Column (8) is the temperature of the electrodeposition bath during deposition. Column (9) is the deposition rate in grams per ampere-hour, a measure of electrodeposition efficiency. Column (10) is the hardness of the coating measured in Vicker's Hardness Number with a 25 gram load, after the substrate and coating have been heat treated for four hours at 600F. In some cases, incipient cracking of the coating was observed either after deposition or after heat treatment, as indicated by a letter c after the hardness value. Column (11) is the rate of thickness increase of the coating during deposition, in micrometers per hour.

Column (12) is a qualitative coating residual stress index, stated in terms of level 1, level 2, or level 3 residual stress index. To obtain the residual stress index, the coating material was electrodeposited onto one side of a thin strip of

-11-

steel about 0.6 inches wide and 1.6 inches long. If after plating the strip was flat or nearly so, the coating was nearly free of residual stress, with a residual stress estimated to be below 30,000 psi (termed Level 1). If after plating the strip had a bowing of about 3-4 millimeters with a residual stress estimated to be below 60,000 psi (termed Level 2). If after plating the strip was bowed more, the residual stress was estimated to be above 60,000 psi (termed Level 3). Level 1 residual stress is acceptable for all applications, while level 2 residual stress is acceptable for some applications. Level 3 residual stress is not acceptable for the coating.

Table I lists acceptable and preferred compositions.

Table I

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
	Curr.						Dep.			Thick.		Resid.
	No.	Dens.	Ni	W	HCA	B	pH	Temp.	Rate	Hard.	Rate	Stress
20	1	0.3	.047c	.21	.23c	.10ba	8.4	120	.482	1033	23	1
	2	0.75	.047c	.21	.23c	.10ba	8.4	120	.255	974	30	1
	3	0.48	.046s	.21	.22c	.12bp	8.4	120	.455	1003	32	1
	4	1.07	.046s	.21	.22c	.12bp	8.5	140	.265	980	45	1
25	5	0.3	.047c	.21	.23c	.11ba	8.6	120	.452	1033	21.5	1
	6	0.3	.047c	.21	.22c	.10ba	8.6	120	.500	989	23.8	1
	7	0.3	.047c	.21	.22c	.10ba	8.5	120	.456	1064	21.7	1
	8	0.3	.047c	.21	.22c	.08ba	8.5	120	.483	1018	23	1
	9	0.3	.046c	.21	.15c	.10ba	8.7	120	.476	940	22.7	1
30	10	0.3	.047c	.21	.26c	.10ba	8.6	120	.495	1033	23.6	1
	11	0.3	.047c	.21	.30c	.10ba	8.6	120	.459	953	21.8	1
	12	0.3	.047c	.15	.22c	.10ba	8.7	120	.443	940	21.1	1
	13	0.3	.030c	.21	.23c	.10ba	8.4	120	.400	920	19.0	1

-12-

Table I (continued)

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
	Curr.						Dep.			Thick.		Resid.
	No.	Dens.	Ni	W	HCA	B	pH	Temp.	Rate	Hard.	Rate	Stress
5	14	0.3	.038c	.21	.22c	.10ba	8.5	120	.403	1115	19.2	1
	15	0.3	.054c	.21	.22c	.10ba	8.5	119	.523	940	24.9	1
	16	0.3	.065c	.30	.31c	.14ba	8.5	120	.496	989	23.6	2
10	17	0.4	.065c	.30	.31c	.14ba	8.4	120	.512	1064	32.5	2
	18	0.5	.065c	.30	.31c	.14ba	8.4	120	.456	1049	36.2	1
	19	0.6	.065c	.30	.31c	.14ba	8.5	120	.408	1033	38.5	2
	20	0.5	.079c	.36	.38c	.17ba	8.5	120	.508	894	40.3	1
	21	0.55	.079c	.36	.38c	.17ba	8.4	120	.461	1064	40	1
15	22	0.6	.079c	.36	.38c	.17ba	8.5	120	.442	974	41.7	1
	23	0.5	.047c	.21	.26t	.10ba	8.5	120	.444	981	34.0	1
	24	0.3	.048c	.21	.22c	.11ba	8.5	120	.434	946	19.8	1
	25	0.5	.046c	.21	.22c	.12bp	6.4	120	.251	1048	19.0	1
	26	0.5	.077s	.35	.37c	.20bp	6.5	121	.237	1064	19.0	1
	27	0.3	.046c	.21	.15c	.10ba	8.7	120	.476	940	22.7	1

Of these acceptable examples, nos. 3, 18, 20, and 21 are most preferred. These specimens plate with low stress, have a thickness buildup of at least 30 microinches per hour, have a deposition rate of at least 0.45 grams per ampere-hour, and have a hardness of at least 900 HV.

The following Table II lists marginal specimens.

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-13-

Table II

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
	Curr.						Dep.	Thick.			Resid.	
No.	Dens.	Ni	W	HCA	B	pH	Temp.	Rate	Hard.	Rate	Stress	
5	28	0.3	.047c	.21	.22c	.15ba	8.7	120	.448	946	21.3	2
	29	0.3	.047c	.21	.23c	.03ba	8.6	120	.492	882	23.4	1
	30	0.3	.047c	.21	.23c	0	8.5	120	.509	894	24.3	1
	31	0.3	.047c	.27	.22c	.10ba	8.6	120	.460	974	21.9	2
	32	0.3	.047c	.28	.29c	.10ba	8.6	120	.403	985	19.2	2
10	33	0.3	.047c	.21	.22c	.10ba	9.1	120	.447	938	21.0	2
	34	0.3	.047c	.21	.22c	.10ba	9.0	100	.390	870	18.6	1

The samples in the marginal group generally electroplate well, but show medium levels of residual stress or are low in the rate of thickness buildup, deposition rate, and/or hardness. Generally, as the composition or deposition conditions depart further from the preferred ranges, more than one parameter deteriorates. In example 28, with boron at the high end, the residual stress increases and the hardness is moderate. In examples 29 and 30, with boron at the low end, the hardness falls to barely acceptable levels. The absence of boron in example 30 causes the sample to become nanocrystalline rather than amorphous. The high tungsten level of example 31 results in increased residual stress in the coating. The elevated tungsten and hydroxycarboxylic acid levels of example 32 result in reduced deposition rate and rate of thickness increase, as well as increased residual stress. The high pH of example 33 causes increased plating stress and moderated hardness. The reduced plating temperature of example 34 lowers the deposition rate and rate of thickness buildup, and reduces the hardness significantly.

-14-

Table III lists unacceptable electrodeposition bath compositions and/or conditions.

Table III

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
	Curr.			Dep.				Thick.			Resid.	
No.	Dens.	Ni	W	HCA	B	pH	Temp.	Rate	Hard.	Rate	Stress	
35	0.7	.047c	.21	.22c	.10ba	8.4	160	.398	946	44.3	2c	
36	0.3	.055c	.21	.22c	.10ba	8.6	120	.520	824	24.8	2	
37	0.3	.064c	.21	.22c	.10ba	8.5	120	.521	858	24.8	3	
10 38	0.3	.039c	.21	.22c	.10ba	8.6	120	.374	960	17.8	2	
39	0.3	.035c	.21	.22c	.075ba	8.6	120	.401	803	19.1	1	
40	0.3	.047c	.21	.23c	.016ba	8.6	120	.492	790	23.4	3	
41	0.3	.047c	.21	.23c	.05ba	8.5	120	.494	835	23.5	1	
42	0.3	.047c	.21	.22c	.10ba	8.4	140	.507	782	24.2	3c	
15 43	0.5	.032c	.14	.17t	.07ba	8.9	120	.239	960	19.0	2	
44	0.8	.032c	.14	.17t	.07ba	8.9	180	.445	907	35.3	2	
45	0.3	.030c	.21	.22c	.10ba	8.5	120	.336	1003	16.0	1	

Example 35 demonstrates that increasing the current density and temperature produces a marginal deposition rate and results in high stress and cracking of the coating. As shown in examples 36 and 37, increased nickel content results in low hardness and increasing residual stress. Low nickel content results in low deposition rate and low rate of thickening, and increased stress, as shown in example 38. Example 39 shows that low nickel and boron produce a coating having a low hardness. A very low boron content is worse than no boron, since the residual stress is very high and the hardness is low, example 40.

A low boron content results in improved, but

-15-

still low, hardness, example 41. Example 42 shows that lower deposition temperature yields an acceptable deposition rate, but high residual stress in the coating and low hardness. In example 42, a 5 lower concentration bath with tartrate as the hydroxycarboxylic acid produces a low deposition rate and high residual stress. Example 44 utilizes a high deposition temperature and current density to improve deposition rate and rate of thickening, but also 10 results in a high residual stress. Operation at 180F is also more difficult than at lower temperatures. Example 45 illustrates the effect of excessively low nickel content. The deposition rate and the rate of thickness buildup of the coating are very low.

15 Figure 3 is an X-ray diffraction pattern, using copper K-alpha radiation, of the coating of Example 24, a mixed amorphous and nanocrystalline coating. There is a short, wide peak at about 44 degrees two-theta, corresponding to nearest neighbor 20 diffraction, and a broad secondary peak at 70-80 degrees two-theta, corresponding to second-nearest neighbor diffraction. This X-ray diffraction structure is to be contrasted with that of Figure 4, for the coating of Example 30. This coating has a 25 nanocrystalline structure. There is a first crystalline peak at about 44 degrees two-theta and a second crystalline reflection at about 50 degrees two-theta due to (211) reflections. A further peak is found at 75 degrees two-theta. The principal peak 30 is nominally 1.5 degrees wide at half height, corresponding to a crystallite size of about 7 nanometers. Figure 5, presented for comparison, is the X-ray diffraction pattern of Example 45, which is fully crystalline and has sharp X-ray diffraction 35 peaks.

Although particular embodiments of the invention have been described in detail for purposes

-16-

of illustration, various modifications may be made without departing from the spirit and scope of the invention. Accordingly, the invention is not to be limited except as by the appended claims.

-17-

Claims

1. An electrodeposition process for depositing a nickel-tungsten coating onto a substrate, comprising the steps of:

5 preparing an electrodeposition bath comprising in solution

from about 0.034X to about 0.047X moles per liter of nickel,

10 from about 0.15X to about 0.28X moles per liter of tungsten,

from about 0.13X to about 0.43X moles per liter of hydroxycarboxylic acid, and

15 boron in an amount selected from the group of zero boron and from about 0.077X to about 0.15X moles per liter of boron,

where X is a scaling factor that can range from about 0.67 to about 1.7 and the bath has a pH of from about 6 to about 9; and

20 electrodepositing a coating onto a substrate from the electrodeposition bath.

2. The process of claim 1, wherein the bath has a composition of about 0.046X moles per liter of nickel, about 0.21X moles per liter of tungsten, about 0.23X moles per liter of hydroxycarboxylic acid, and about 25 0.11X moles per liter of boron.

3. The process of claim 1, wherein the nickel is supplied by a nickel-containing constituent selected from the group consisting of nickel carbonate, nickel sulfate, nickel chloride, nickel oxide, and combinations thereof.

30 4. The process of claim 1, wherein the tungsten is supplied by a tungsten-containing constituent selected from the group consisting of sodium tungstate, ammonium tungstate, ammonium meta tungstate, tungstic acid, and

-18-

combinations thereof.

5. The process of claim 1, wherein the hydroxycarboxylic acid is supplied by a constituent selected from the group consisting of ammonium citrate and ammonium tartrate.

10. The process of claim 1, wherein the boron is supplied by a constituent selected from the group consisting of boric acid, boron phosphate, and combinations thereof.

15. The process of claim 1, wherein the step of electrodepositing is accomplished at a temperature of from about 100F to about 140F.

20. The process of claim 1, wherein the step of electrodepositing is accomplished at a cathodic current density of from about 0.3 amperes per square inch to about 1.2 amperes per square inch.

25. The process of claim 1, including the additional step, after the step of electrodepositing, of heating the coated substrate to a temperature of from about 400F to about 700F.

30. The process of claim 1, wherein the electrodeposition bath further comprises a substance selected from the group consisting of a leveling agent, a brightening agent, and a wetting agent.

35. A substrate having a coating prepared by the process of claim 1.

40. An electrodeposition process for depositing a nickel-tungsten coating onto a substrate, comprising the steps of:

45. preparing an electrodeposition bath comprising in solution from about 0.034X to about 0.047X moles per liter of nickel, the nickel being provided by a bath addition of a nickel-containing constituent selected from the group consisting of nickel carbonate, nickel

-19-

sulfate, nickel chloride, nickel oxide, and combinations thereof,

from about 0.15X to about 0.28X moles per liter of tungsten, the tungsten being provided by a
5 bath addition of a tungsten-containing constituent selected from the group consisting of sodium tungstate, ammonium tungstate, ammonium meta tungstate, tungstic acid, and combinations thereof,

10 from about 0.13X to about 0.43X moles per liter of hydroxycarboxylic acid, the hydroxycarboxylic acid being provided by a bath addition of a hydroxycarboxylic acid-containing constituent selected from the group consisting of ammonium citrate and ammonium tartrate, and

15 from about 0.077X to about 0.15X moles per liter of boron, the boron being provided by a bath addition of a boron-containing constituent selected from the group consisting of boric acid, boron phosphate, and combinations thereof,

20 where X is a scaling factor that can range from about 0.67 to about 1.7 and the bath has a pH of from about 6 to about 9; and

electrodepositing a nickel-tungsten-boron coating onto a substrate from the electrodeposition bath.

1/3

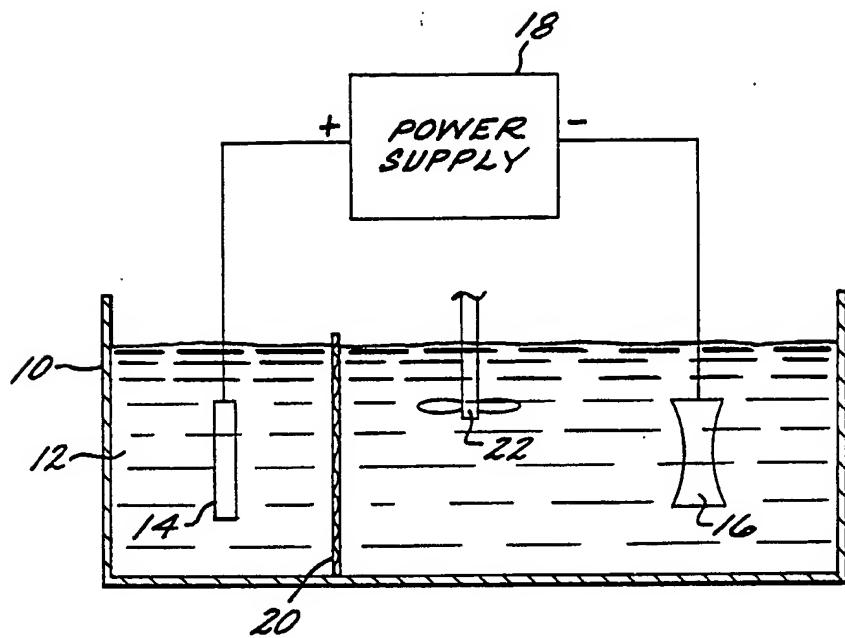


FIG. 1

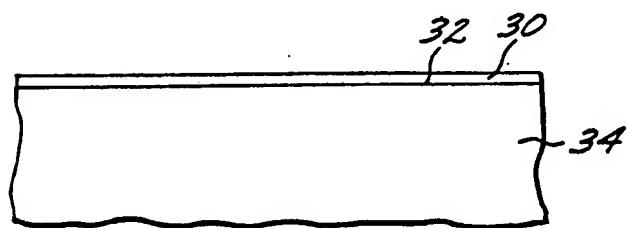


FIG. 2

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2/3

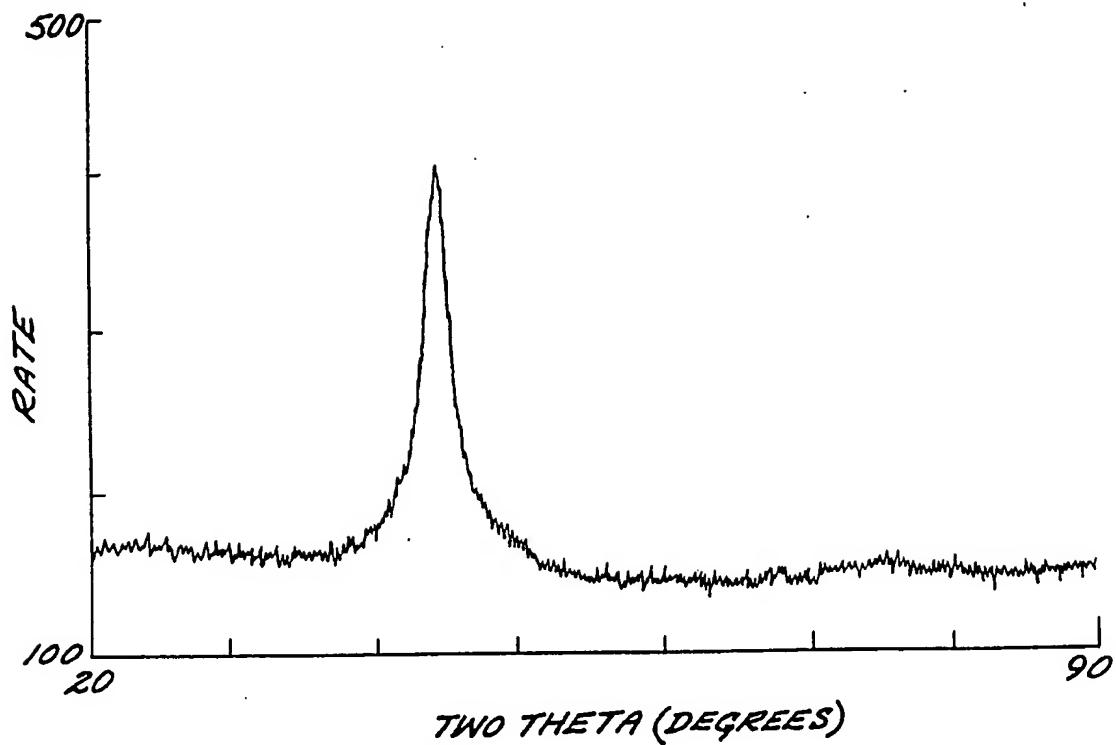
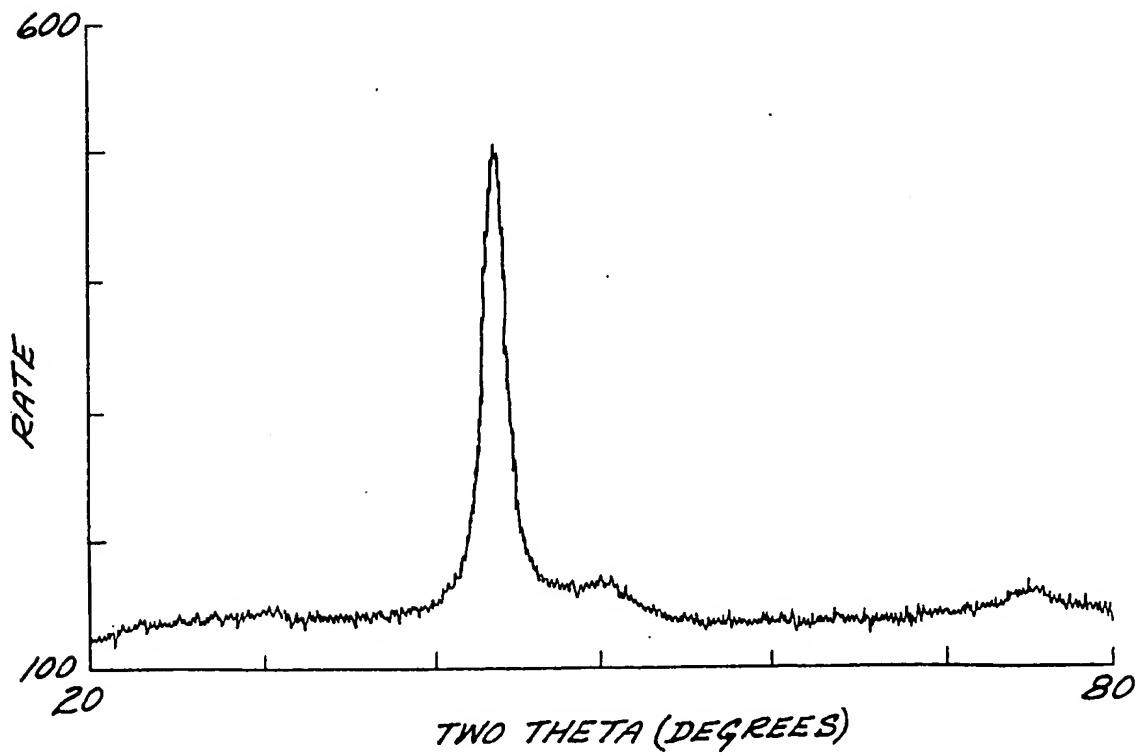


FIG. 3

FIG. 4



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3/3

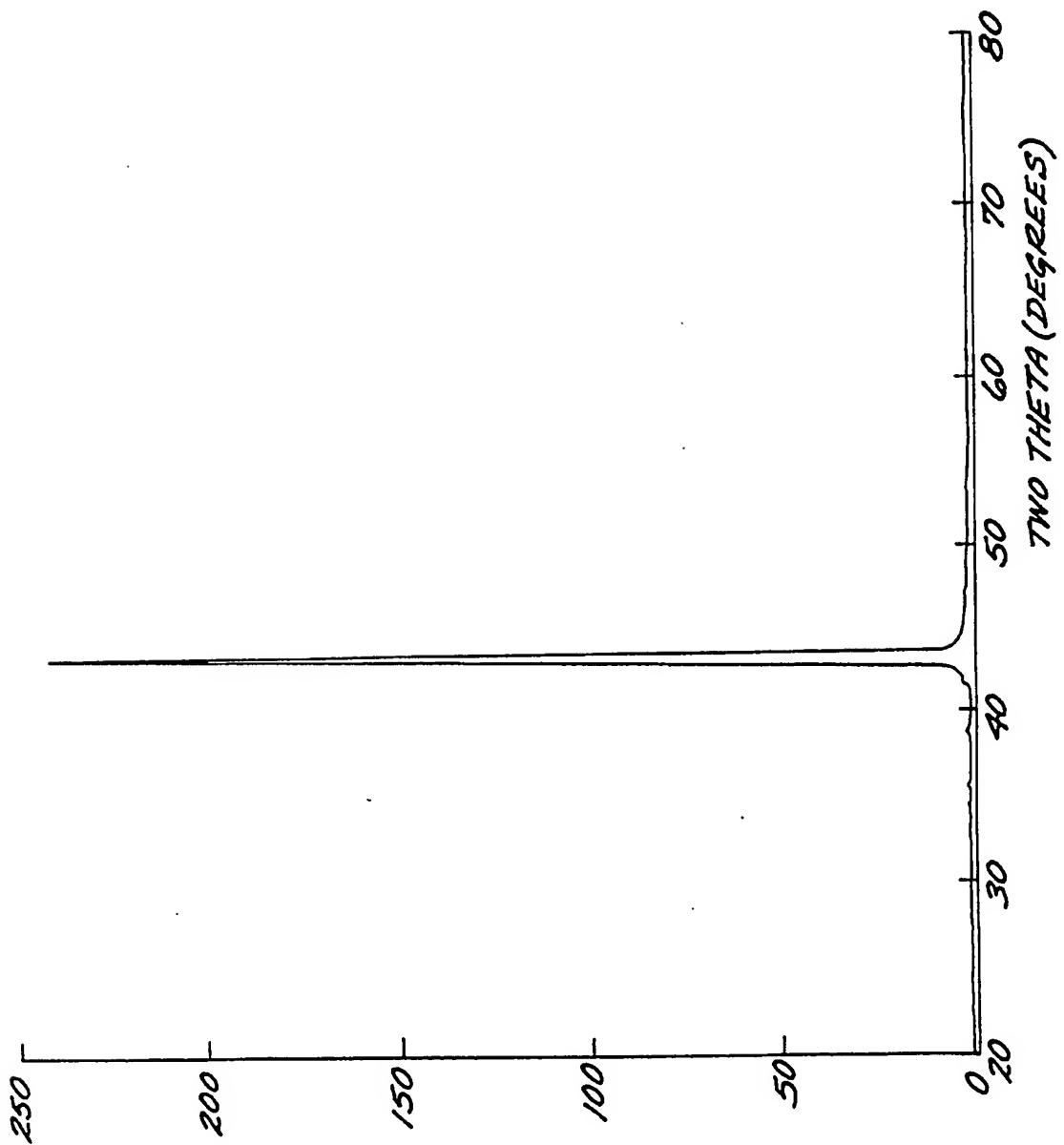


FIG. 5

TOTAL COUNTS X10³

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INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/US 93/12420

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C25D3/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 9, no. 160 (C-289)(1883) 4 July 1985 & JP,A,60 033 382 (NIHON PUREETEINGU K.K.) 20 February 1985 see abstract</p> <p>---</p>	
A	<p>FR,A,789 883 (ARMSTRONG) 7 November 1935 see page 5; example 1</p> <p>---</p>	
A	<p>US,A,4 529 668 (CROOPNICK) 16 July 1985 cited in the application</p> <p>-----</p>	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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1

Date of the actual completion of the international search

15 April 1994

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No

PCT/US 93/12420

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-789883		BE-A- 414790 BE-A- 416235 CH-A- 282704 CH-A- 285458 CH-A- 289581 CH-A- 289582 DE-C- 654270 DE-C- 683879 DE-C- 941190 FR-E- 59392 FR-A- 809371 FR-A- 989933 GB-A- P3266 GB-A- P3267 GB-A- 460840 GB-A- 460886 GB-A- 460931 GB-A- 477519 GB-A- 682878 GB-A- 682879 GB-A- 941190 IT-A- 482373 NL-C- 76882 NL-C- 79528 US-A- 2145241 US-A- 2145745 US-A- 2160322 US-A- 2599867 US-A- 2681299	
US-A-4529668	16-07-85	AU-B- 564336 AU-A- 4406085 CA-A- 1251761 EP-A, B 0181927 JP-T- 61502263 WO-A- 8505382	06-08-87 13-12-85 28-03-89 28-05-86 09-10-86 05-12-85